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AUTHOR(S)

PHILIP BOUDJOUK

PERFORMER

DEPARTMENT OF CHEMISTRY
NORTH DAKOTA STATE UNIVERSITY
FARGO, ND 58105-5516

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This report summarizes progress of research in five major areas supported by the Air Force Office of Scientific Research: 1) Strained Organosilicon Systems, 2) Reactive Intermediates Containing Silicon, 3) Silicon Selenides, 4) Organosilicon Sonochemistry, and 5) New Catalytic Processes Involving Silicon.

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SENIOR RESEARCH PERSONNEL: Dr. Jerome Knoblich
Dr. Daryl Osterkamp
Dr. Carolyn Osterberg

JUNIOR RESEARCH PERSONNEL: Mr. Steven Bahr
Mr. Eric Black
Mr. Brian Hauck
Mr. John Jacobsen
Mr. Rajkumar Kumarathanan
Mrs. Amirthini B. Rajkumar
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56. "A Convenient, Naphthalene-Catalyzed Synthesis of Alkali Metal Selenides and Diselenides in Tetrahydrofuran and the Reactivity Differences Exhibited by These Salts Toward Organic Bromides. Effect of Ultrasound." D.P. Thompson and P. Boudjouk, J. Org. Chem., 53, (1988) 2109.
57. "Convenient Routes to Di-t-Butylsilylene: Chemical, Thermal and Photochemical Generation", P. Boudjouk, U. Samaraweera, R. Sooriyakumaran, J. Chrusciel and K.R. Anderson, Angew. Chem., Intl. Ed., 27, (1988) 1355.
58. "Reductive Coupling of Carbonyls with Zinc and Trimethylchlorosilane to Produce O-Silylated Pinacols. The Effect of Ultrasound." J.-H. So, M.-K Park and P. Boudjouk, J. Org. Chem., 53, (1988) 5871.
59. "A New Catalyst for the Efficient and Selective β -Hydrosilation of Acrylonitrile. Effect of Ultrasound." A.B. Rajkumar and P. Boudjouk, Organometallics, 5, (1989) 549.
60. "Convenient Syntheses of Hexamethyldisilthiane and Tetramethyldisilthiane", J.-H. So and P. Boudjouk, Synthesis, (1989) 306.

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61. "Inorganic and Organometallic Synthesis with Ultrasonic Waves." P. Boudjouk, Comments on Inorganic Chemistry 1990, Vol. IX, 123; F. Basolo and P. Gülich, Eds., Gordon and Breach Publ. London.
62. "Dehydration of Metal Hydrates with Trimethylchlorosilane. A Simple and Convenient Route to Anhydrous Complexes." P. Boudjouk and J.-H. So, Inorg. Chem., 29, (1990) 1592.
63. "Potassium Fluoride Activated Alcoholysis of Hindered Siliranes" R. Kumarathan and P. Boudjouk, Tetrahedron Lett., 31, (1990) 3987.
64. "Synthesis of The First Stable 1,2-Silathietane." P. Boudjouk and U. Samaraweera, Organometallics, 9, (1990) 2205.
65. "Chemical Reactivity of Metal Particles Produced by Laser Ablation into Liquids", W. L. Parker and P. Boudjouk, Mat. Res. Soc. Symp. Proc. 191, (1990) 103.
66. "The Structure of 1,1,3,3,5,5 Hexaphenylcyclotrisilselanane", W. L. Parker, D. E. Thompson, S. R. Bahr and P. Boudjouk, Acta Cryst. in press.
67. "Spectroscopic Detection of New Surface Species on Activated Nickel Particles", W. L. Parker, P. Boudjouk, and A. B. Rajkumar, J. Am. Chem. Soc. in press.
68. "Nickel Catalyzed Dehydrogenative Coupling of Phenylsilanes" P. Boudjouk, A. B. Rajkumar and W.L. Parker, J. Chem. Soc., Chem. Commun., in press.
69. "Cyclosilselenanes. Photochemical and Thermal Precursors of Silaneselones, Reactive Intermediates Containing the Silicon-Selenium Double Bond." P. Boudjouk, S.R. Bahr and D.P. Thompson Organometallics, in press.
70. "Anhydrous Metal Chlorides", J.-H. So and P. Boudjouk, Inorganic Syntheses, Vol. 29, in press.
71. "Hexamethyldisilthiane", J.-H. So and P. Boudjouk, Inorganic Syntheses, Vol. 29, in press.
72. "New Developments in the Chemistry of Silicon Selenides", P. Boudjouk, Polyhedron, Symposium in Print: Homopolyatomic Silicon, Germanium and Tin Chemistry, in press.
73. "Nickel Catalyzed Hydrosilylation Reactions", P. Boudjouk, B.-H. Han and J. R. Jacobsen, submitted.
74. "1,1 Di-t-butylsilirane. Synthesis and Characterization of the First Silirane Without Substituents on the Ring Carbons", P. Boudjouk, E. Black and R. Kumarathan, submitted.
75. "Hydride Abstraction from Siloles: Routes to Potentially Anti-Aromatic Species." P. Boudjouk, A.B. Rajkumar, J. Lambert, W. Schilf, M.S. Gordon, and K. Nguyen, Organometallics, to be submitted.

Book Chapters

1. "Heterogeneous Sonochemistry", in Ultrasound: Chemical, Physical and Biological Effects, K. S. Suslick Ed., Verlag Chemie International, 1988.
2. "Organosilicon Chemistry - A Brief Overview" with T. J. Barton in Silicon-Based Polymer Science. A Comprehensive Resource, Advances in Chemistry Series No. 224, J. Ziegler, Ed., American Chemical Society, Wash., DC, 1990.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Five major areas of research at North Dakota State University have been supported by the Air Force Office of Scientific Research: 1) Strained Organosilicon Systems, 2) Reactive Intermediates Containing Silicon, 3) Silicon Selenides, 4) Organosilicon Sonochemistry, and 5) New Catalytic Processes Involving Silicon. Objectives and accomplishments in each of these areas is summarized below:

1) Strained Organosilicon Systems: We have successfully prepared very stable three-membered rings containing silicon and two carbon atoms. By attaching large groups to the silicon atom we have been able to produce these ring systems with minimal substitution on the ring carbon atoms. This allowed definitive structural characterization, by nuclear magnetic resonance spectroscopy, of the simplest members of this family. The simplicity of these systems has also permitted successful investigation of insertion and fragmentation reactions that lead to precursors to metal silicides, silicon selenides and silicon carbides. Very recently we developed a method of using the silirane as a very simple and efficient precursor to a robust protecting group.

2) Reactive Intermediates Containing Silicon: During the tenure of this grant period we have greatly improved access to one of the most important of silicon containing reactive intermediates, di-*t*-butylsilylene ($t\text{-Bu}_2\text{Si:}$) and took big steps towards the understanding of the mechanisms of reactions used to generate the species as well as those mechanisms of reactions in which it participates. It is now possible to produce this intermediates thermally at moderate temperatures and photochemically at room temperature. This intermediate will play an important role in building highly reactive silicon-metal fragments.

3) Silicon Selenides: Under this grant we have produced the first examples of compounds containing the silicon-selenium double bond. These reactive molecules dimerize and trimerize to give novel cyclic compounds that pyrolyze to form silicon selenide. The work was extended to tin and we developed an excellent synthesis of ultrapure tin selenide crystals. We examined the thermal and photochemical reactions of these cyclic silicon

selenides and found them to be useful precursors to a variety of heterocycles.

4) Organosilicon Sonochemistry: We continue to explore the uses of ultrasound in facilitating the reactions of organometallic compounds, in particular those involving organosilanes. The reductive coupling of carbonyl compounds in the presence of zinc was greatly accelerated by ultrasound leading to very good yields of symmetrical and unsymmetrical olefins as well as "pinacol" products.

5) New Catalytic Processes Involving Silicon: Our work in ultrasound was instrumental in developing two new catalytic processes. We prepared an extremely active form of nickel using ultrasound that is an efficient catalyst for the hydrosilation reaction. During the course of this grant period we examined the surface of the nickel using Scanning Electron Microscopy and Raman Spectroscopy and identified the presence of carbonyl species. We also determined that these species are essential to the catalysis reaction. This is the first example of nickel catalyzed hydrosilation and our process is being evaluated as a possible replacement for the currently used chloroplatinic acid. We have also developed a new catalyst for exclusive β hydrosilation of acrylonitrile. There are very few catalysts that perform this task well. Ours is about four times as effective as known systems. It is also being evaluated for commercial use.

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Title Page

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AFOSR Grant No. 88-0060

New Approaches to Novel Organosilanes

Philip Boudjouk
Department of Chemistry
North Dakota State University
Fargo, North Dakota 58105

Abstract

This report summarizes progress of research in five major areas supported by the Air Force Office of Scientific Research: 1) Strained Organosilicon Systems, 2) Reactive Intermediates Containing Silicon, 3) Silicon Selenides, 4) Organosilicon Sonochemistry, and 5) New Catalytic Processes Involving Silicon.

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This Annual Technical Report covers the period from November 1, 1987 through October 31, 1990. Our objectives were to advance our knowledge and understanding in five areas of organosilicon chemistry: 1) Strained Organosilicon Systems, 2) Reactive Intermediates Containing Silicon, 3) Silicon Selenides, 4) Organosilicon Sonochemistry, and 5) New Catalytic Processes Involving Silicon.

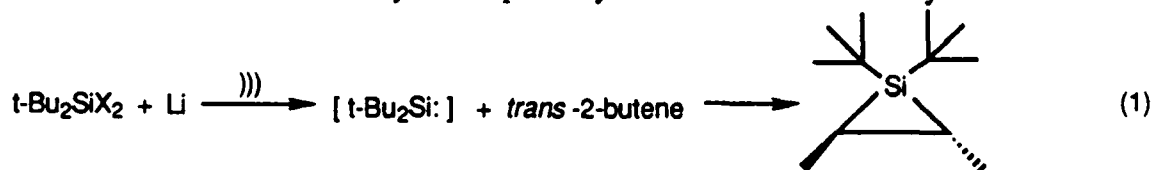
Strained Organosilicon Systems

Siliranes

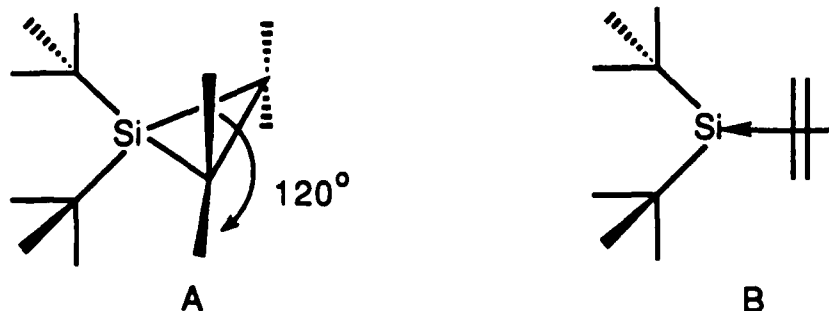
Our efforts on the strained ring area have been focused on three-membered rings. In particular we have been concentrating on siliranes and silirenes such as 1 and 2. The distinguishing feature



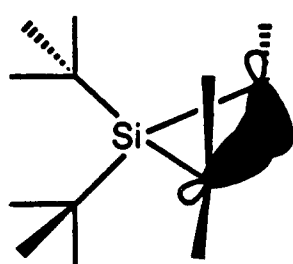
we are exploiting is the use of large groups on silicon to control the reactivity of the ring system. We have prepared a number of these with small groups on the carbon atoms. Access to these siliranes is possible because of a convenient synthetic pathway devised in this laboratory under AFOSR support:



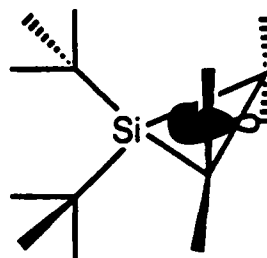
We have recently prepared the first silirane ring system with only hydrogens on the ring carbons. The importance of this development is that it allows, *for the first time*, accurate and precise measurement of the carbon-hydrogen coupling constants in the ring permitting a complete solution structure determination of the silirane ring. Since molecules of this size will not crystallize to permit determination of structure by x-ray crystallography, this result represents a significant advance. In summary we have determined that the H-C-H bond angles are 120° , and that the C_2H_4 fragment is planar as in structure A:



This raises a fundamental bonding question: Does this geometry support a pi-complex type of bond as depicted in B? Extensive calculations by Mark Gordon and his group indicate that most of the electron density in the ring is on the outside in "banana bond" style as shown in C and that very little electron density is *inside* the ring as illustrated in D:

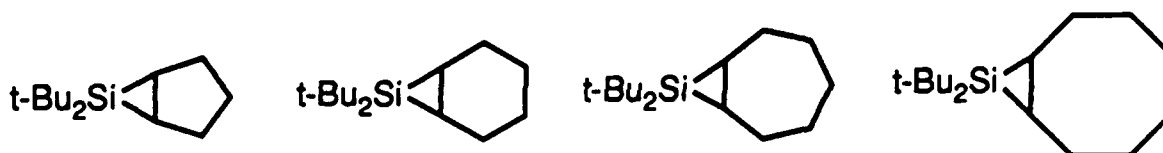


C



D

Our synthetic approach, which employs commercially available reagents, is broadly applicable in that it is useful for a variety of alkenes. Thus we have been able to prepare fused ring siliranes using cycloalkenes in place of 2-butene in eq 1:



These fused ring systems have distinctly different reaction pathways under pyrolytic conditions and yield different products when exposed to insertion reagents such as sulfur and selenium. One surprising result is that the fused cyclopentane is considerably more stable towards thermolysis and insertion than the fused cyclohexane. Ring strain was expected to dominate the chemistry and does not. Why? We are examining that question. We are now preparing silylene adducts of cyclobutenes and cyclopropenes in an effort to fully explore, for the first time, the effect of strain on the fragmentation and insertion reactions of siliranes.

Siliranes-Precursors to Protecting Groups

The strain in the three-membered ring can be put to good use in the presence of nucleophiles. We have developed a method for the high yield ring cleavage of siliranes in the presence of alcohols. Ordinarily, alcohols open the silirane rings with small substituents under very mild conditions but our siliranes with di-*t*-butyl groups on the silicon severely inhibit the reaction. On the other hand, large groups on silicon can provide exceptional stability towards hydrolysis, oxidation, reduction and substitution. We discovered that catalytic quantities of fluoride ion greatly accelerated the

reaction and provided the protected alcohol in very high yields under mild (room temperature, <2 h) conditions (eq 2):



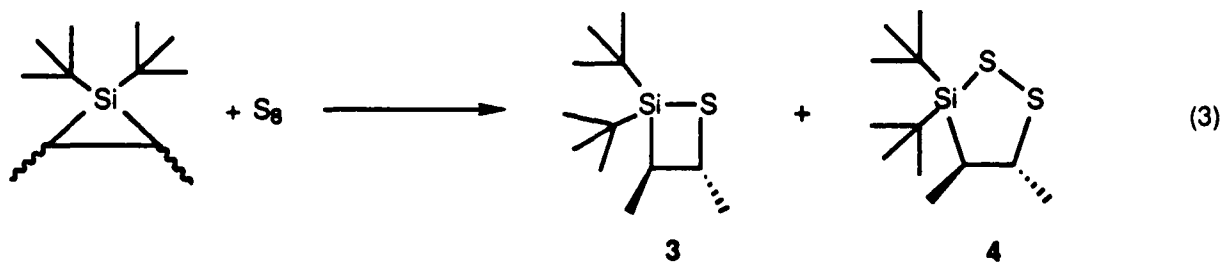
reaction very slow in the absence of fluoride ion

Highly hindered alcohol.
R = n-Bu, cyclohexyl

The di-*t*-butylcyclohexylsilyl protecting group is very bulky and extremely difficult to attach to any atom by any of the conventional substitution mechanisms. The silirane precursor provides access to the silicon atom that would not be available if it were in the usual tetrahedral geometry. How the silirane is activated by the fluoride ion is an important mechanistic question. We are pursuing this avenue of investigation. More recently we discovered that the reaction is greatly accelerated if we add small amounts of crown ether to complex the potassium ion. We now observe reaction rates of less than 1 hr at room temperature if only 10% of crown ether is added to the reaction mixture.

Silthietanes

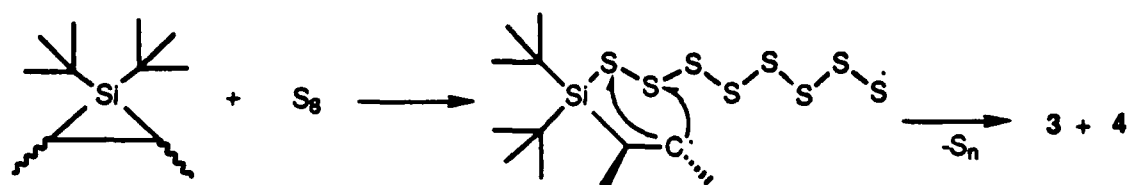
The combination of ring strain and steric hindrance at the silicon has led to unexpected reactivity patterns. The "protecting group" reaction in eq 2 is one example. Still another is the reaction of siliranes like **1** with sulfur. To our surprise, siliranes will permit the insertion of only one sulfur atom to produce the first *stable* examples of the new ring systems, 1,2-silthietanes.¹ The disulfur product is also obtained (eq 3):



There is a loss of stereochemistry in this reaction. We obtain the same products from both the *cis* and *trans* silirane leading us to postulate the following mechanism (Scheme 1):

Scheme 1

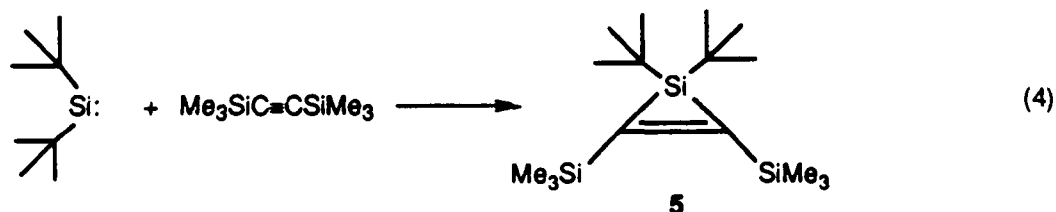
¹P. Boudjouk, U. Samaraweera, submitted for publication



The conversion to the *trans* isomer of the products is favored because of reduced steric interactions compared to the *cis* isomer. The radical intermediates permit bond rotation to the more stable configuration before ring closure to 3 and 4. If the reaction were concerted, the geometry of the starting silirane would be preserved.

Silirenes

Fragmentation of siliranes under mild conditions is an important part of our work on this ring system. The goal is to develop a very mild method of delivering the di-*t*-butylsilylene intermediate to reagents that won't stand up to vigorous reaction conditions. We have had some success in this area. We have been able to generate di-*t*-butylsilylene from 1 in the presence of bis(trimethylsilyl)-acetylene producing the very stable silirene 5 in good yield (eq 4):



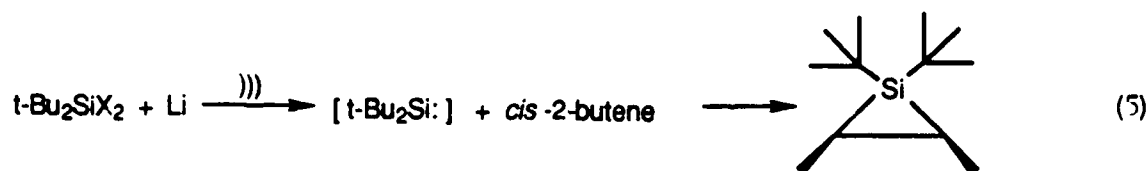
We are just beginning our investigation of the insertion and fragmentation reactions of this compound. The presence of the double bond opens the possibility for complexation to transition metals prior to insertion. Our plan is to try and use 5 as a precursor to the first stable silametallo-cyclobutenes. The stability 5 and the absence of phenyl groups should allow us to more easily probe the electronic properties of this ring system.

Reactive Intermediates Containing the Di-*t*-butylsilyl Group

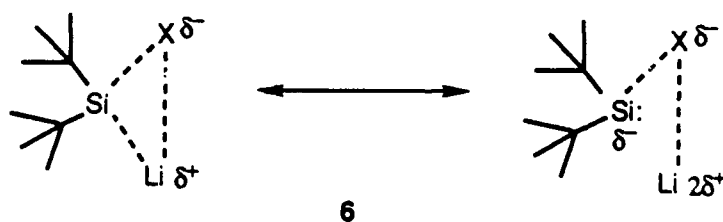
Di-*t*-butylsilylene

Silylenes are at the forefront of research in organosilicon chemistry. Developing mild methods of producing these intermediates is one of the biggest challenges to workers in this field. We have focused on this problem and have developed very mild routes to one of the most interesting and useful silylenes: di-*t*-butylsilylene. We have reported two convenient routes to this reactive intermediate, both of which offer some promise of being applicable to other silylenes, in particular, those with large groups on the silicon.² The first of these two routes employs commercially available reagents di-*t*-butyldichlorsilane and lithium (eq 5):

²P. Boudjouk, U. Samaraweera, R. Sooriyakumaran, J. Chrusciel and K. Anderson, *Angew. Chem., Int. Ed. Engl.* 1988, 27, 5555.



One of the key features of this reaction is that the stereochemistry of the *cis*-2-butene is preserved upon reaction with the silylene. This argues strongly for a singlet ground state for the silylene since triplet carbene species are known to lead to a mixture of *cis* and *trans* cyclopropanes. The sila-cyclopropane **1** is also a very useful precursor for di-*t*-butylsilylene. The ability to generate this intermediate from two very different sources: the first, eq 5, from any di-*t*-butyldihalosilane and a Group 1 metal in a polar solvent like tetrahydrofuran and the second, *via* pyrolysis of **1** in a wide choice of solvents has permitted us to gain some mechanistic insights into the overall process of metal-halogen exchange at silicon centers. In summary, we now have very persuasive evidence that a "silylenoid" species like **6** is important in eq 5.



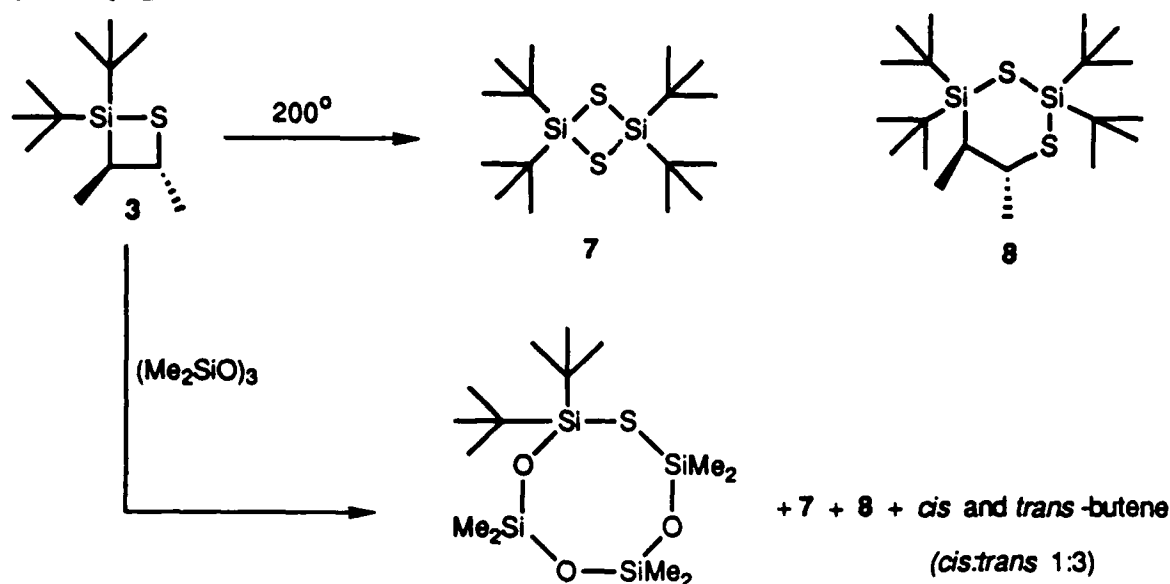
Our work is moving in the direction of examining this exchange and elimination sequence for smaller groups on silicon with the goal of shedding light on the critically important mechanisms involved in the synthesis of polysilanes. Polysilanes are essential polymers in the design of many new materials but suffer from a dearth of synthetic approaches. The reaction of Group I metals with dihalo and trihalosilanes is the only viable route to these polymers yet very little is understood about the mechanism of reaction.

Di-*t*-butylsilylithione

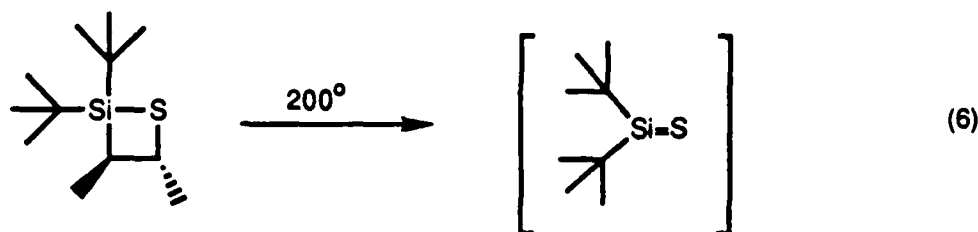
Silylthiones are species that possess a double bond between silicon and sulfur. Only a few examples of these reactive intermediates are known.³ We found that pyrolysis of the 1,2 silylthietanes discussed above leads to products derived from this species (Scheme 2).

³ a) Sommer, L. H. ; McLick,

Scheme 2



Very likely the first step in the reaction is the cleavage of 3 to form the highly reactive di-*t*-butylsilthione (eq 6):



This is the first example of a silthione with bulky groups on the silicon and it raises the possibility of studying the intermediate under a broader variety of conditions than for the smaller more reactive species. Very little is known about silthiones in general and one of our goals is to explore its chemistry.

Silicon Chalcogenides

Disilthianes

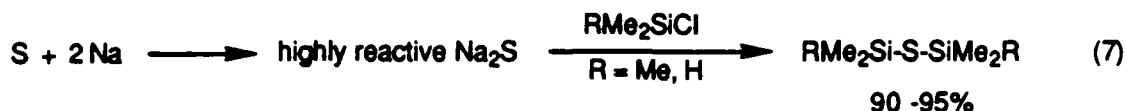
Hexamethyldisilthiane (9) has been widely used in organic synthesis as a sulfur transfer agent.⁴ While there are several routes to 9, even the best known procedures have inconvenient aspects such as requiring a toxic starting material like hydrogen sulfide⁵, or a very expensive one such as lithium triethylborohydride⁶. By adapting a procedure we developed for producing activated metals,⁷ i.e.,

⁴ Berwe, H.; Haas, A., *Chem. Ber.* **1987**, *120*, 1175.

⁵ Harpp, D.N.; Steliou, K. *Synthesis* **1976**, 721.

sonicating metal halides in the presence of an alkali metal to give highly dispersed metal powders, we prepared alkali metal sulfides in high yield and in an activated form.

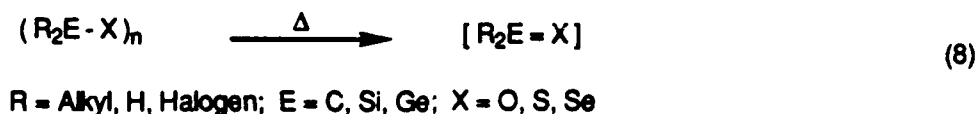
This permitted efficient reaction with trimethylchlorosilane to give excellent yields of the disilthiane 9 (R = Me) and its lighter analog 8 (R = H) (eq 7).



The synthesis is easily scaled up and will permit a more thorough investigation of the utility of this reagent in inorganic as well as organic systems.

Cyclic Silselenanes, Precursors to Silaneselones

Pyrolysis of cyclic compounds of the type $(\text{R}_2\text{E-X})_n$, $n = 2, 3, 4$ is a well-known route to reactive intermediates of the type $\text{R}_2\text{E=X}$, (eq 8).⁸ This approach has been used to generate reactive intermediates for $\text{E} = \text{C}$ and $\text{X} = \text{S}, \text{Se}$ such as thiocarbonyl fluoride,⁹ thioacetaldehyde and thioacetone,¹⁰ thioformaldehyde,¹¹ and selenoacetaldehyde¹² as well as for some of the heavier analogs like dimethylsilathione ($\text{R} = \text{Me}, \text{E} = \text{Si}, \text{X} = \text{O}$)^{13,14} and diethylgermathione ($\text{R} = \text{Et}, \text{E} = \text{Ge}, \text{X} = \text{S}$)¹⁵.



⁶ Detty, M. R.; Seidler, J. *Org. Chem.* **1982**, *47*, 1354.

⁷ Boudjouk, P.; Thompson, D. P.; Ohrbom, W. H.; Han, B.-H. *Organometallics*, **1986**, *5*, 1257.

⁸ For reviews on heavy atom analogues of ketones see:

a) Guziec, J.C. in *Organoselenium Chemistry*, Liotta, D., Ed.; John Wiley and Sons: New York, **1987**, 237.

b) Raabe, C.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

c) Satge, J. *Pure Appl. Chem.* **1984**, *56*, 137.

⁹ Kroto, H.W.; Suffolk, R.J. *Chem. Phys. Lett.* **1972**, *17*, 213.

¹⁰ Kroto, H.W.; Landsberg, B.M.; Suffolk, R.J.; Vodden, A. *Chem. Phys. Lett.* **1972**, *29*, 265.

¹¹ Block, H.; Hirabayashi, T.; Mohmand, S.; Solouki, B. *J. Amer. Chem. Soc.*, **1982**, *104*, 3119.

¹² Hutchinson, M.; Kroto, H.W. *J. Mol. Spect.*, **1978**, *70*, 347-356.

¹³ Weber, W.P.; Soysa, H.S.D. *J. Organomet. Chem.*, **1979**, *165*, C1.

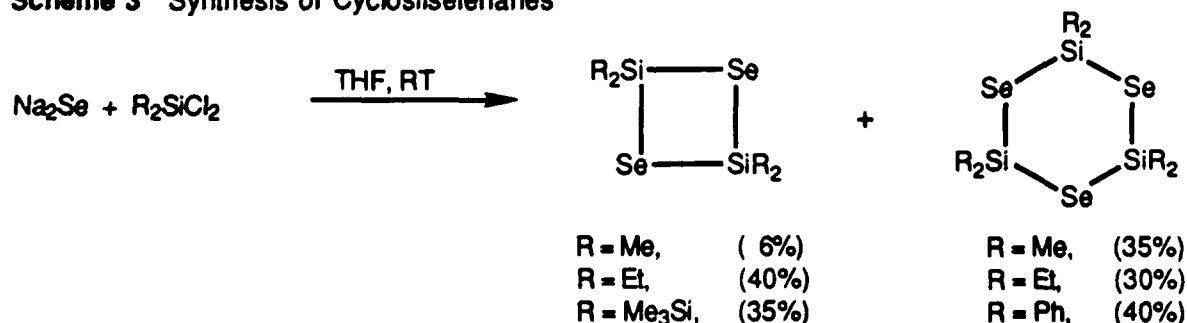
¹⁴ Moedritzer, K. *J. Organomet. Chem.* **1970**, *21*, 315.

¹⁵ Lavayssiere, H.; Dousse, G.; Barrau, J.; Satge, J.; Bouchart, M. *J. Organomet. Chem.* **1978**, *161*, C59.

The first cyclosilselenanes were prepared by Schmidt and Ruf in 1963¹⁶ but no attempts to generate silaneselones from these compounds, with the exception of our own, have been reported. Recently we described a convenient procedure for the synthesis of alkali metal selenides and diselenides in THF from an alkali metal and selenium in the presence of a catalytic amount of naphthalene.¹⁷ Using sodium selenide produced by this technique we prepared tetraethylcyclodisilselenane and hexaethylcyclotrisilselenane and found that photolysis (254 nm) of the latter generated diethylsilaneselone, a reactive intermediate containing the silicon-selenium double bond.¹ We have prepared several new cyclosilselenanes and investigated some of their photochemical and thermal reactions.

When R_2SiCl_2 ($R = Et, Me$) is added to sodium selenide, generated *in situ* from selenium and sodium in the presence of a catalytic amount of naphthalene, cyclodi- and cyclotrisilselenanes are produced (Scheme 3). Tetramethylcyclodisilselenane is a solid in pentane at -78° and a light yellow oil at room temperature. Although it only slowly decomposes in solution, isolated samples will decompose in minutes even under a nitrogen atmosphere. Hexamethylcyclotrisilselenane, tetraethylcyclodisilselenane and hexaethylcyclotrisilselenane were isolated as yellow oils in $>90\%$ purity by molecular distillation. These compounds are unstable in air but withstand room temperature under nitrogen for several hours and can be stored in a hydrocarbon solvent at 0° for months. The only isolated product of the reaction of sodium selenide with diphenyldichlorosilane is hexaphenylcyclotrisilselenane. This compound is a colorless, crystalline solid which is stable for several hours in the presence of dry air. The reaction of bis(trimethylsilyl)dichlorosilane with sodium

Scheme 3 Synthesis of Cyclosilselenanes



selenide produces tetrakis(trimethylsilyl)cyclodisilselenane, isolated as light green needles which are stable in dry air for several days.

Ring Contractions of Cyclotrisilselenanes

$(Me_2SiSe)_3$ and $(Et_2SiSe)_3$ undergo ring contraction photochemically and thermally to form $(Me_2SiSe)_2$ and $(Et_2SiSe)_2$ respectively (Table I). The UV spectra of $(Me_2SiSe)_3$ and $(Et_2SiSe)_3$

¹⁶Schmidt, V.M.; Ruf, H.F.; *Z. Anorg. Allg. Chem.* **1963**, *53*, 2109.

¹⁷Thompson, D.P.; Boudjouk, P. *J. Org. Chem.* **1988**, *53*, 2109.

Table I Ring Contractions of $(\text{Me}_2\text{SiSe})_3$ and $(\text{Et}_2\text{SiSe})_3$

$(\text{R}_2\text{SiSe})_3 \longrightarrow (\text{R}_2\text{SiSe})_2$					
Entry	R	Conditions	Time	% Yield ^a of $(\text{R}_2\text{SiSe})_2$	% Conversion
1	Me	254 nm/hexane	23 h	68	95
2	Me	150°/decane	48 h	~3	~3
3	Me	225°/decane	70 h	39	46
4	Me	225°/decane	94 h	35	48
5	Et	254 nm/hexane	18 h	90	100
6	Et	225°/decane	40 h	80	100
7	Et	155°/decane	40 h	15	16

^a Yields determined by glc

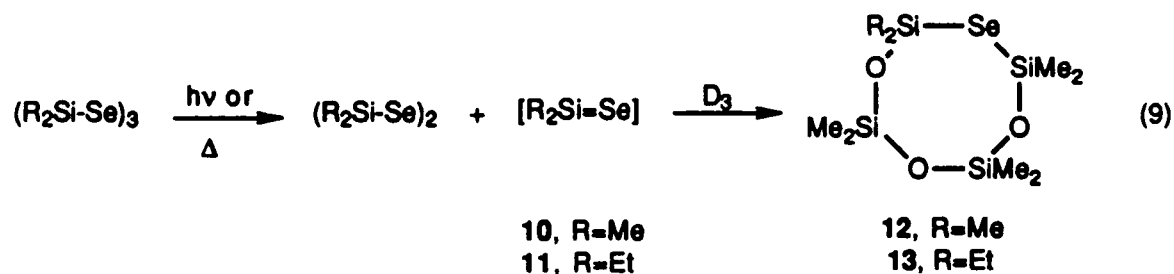
show absorbances at 254 nm, while the absorbances of $(\text{Me}_2\text{SiSe})_2$ and $(\text{Et}_2\text{SiSe})_2$ cut off at 220 nm. Photolysis (Rayonet, 254 nm lamps, hexane) of $(\text{Et}_2\text{SiSe})_3$ produces $(\text{Et}_2\text{SiSe})_2$ in 90% yield and is the only product observed by GC (Table I, entry 5). In a separate experiment, it was shown that $(\text{Et}_2\text{SiSe})_2$ is essentially inert to photolysis (254 nm, 48 h, 93% recovery, no evidence of $(\text{Et}_2\text{SiSe})_3$). Photolysis of $(\text{Me}_2\text{SiSe})_3$ produces $(\text{Me}_2\text{SiSe})_2$ in 68% yield (Table I, entry 1). Decomposition was observed in the form of discharged elemental selenium in all reactions, photochemical and thermal.

Replacing methyl groups with ethyl groups significantly alters the chemistry of the ring systems. For example, $(\text{Me}_2\text{SiSe})_2$ has a $t_{1/2}$ of 60 hours at 69° (refluxing hexane) producing a 22% yield of $(\text{Me}_2\text{SiSe})_3$, whereas $(\text{Et}_2\text{SiSe})_2$ is stable indefinitely at that temperature and even after 32 h at 250°, 80% can be recovered (no $(\text{Et}_2\text{SiSe})_3$ was detected). For the six-membered rings, the stabilities are reversed: $(\text{Me}_2\text{SiSe})_3$ is stable to 110°, is only 3% converted to $(\text{Me}_2\text{SiSe})_2$ at 150°, and is less than 50% converted at 225° even after 94 hours (Table I, entries 1, 6 and 7). The ethyl analogue $(\text{Et}_2\text{SiSe})_3$, on the other hand, shows much higher conversion rates to $(\text{Et}_2\text{SiSe})_2$ thermally and photochemically (Table I, entries 2-4). Photolysis of $(\text{Me}_2\text{SiSe})_3$ at 254 nm in hexane produces a mixture of $(\text{Me}_2\text{SiSe})_2$ and $(\text{Me}_2\text{SiSe})_3$ in an 11 to 1 ratio. This mixture was then transferred to a sealed tube and heated to 225°. After 36 h the ratio changes to about 5.3 to 1 but significant quantities of elemental selenium were also produced.

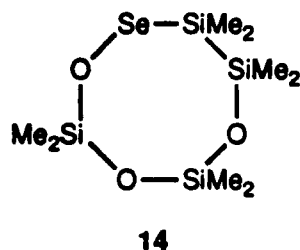
Thus only for the methyl case does there appear to be an equilibrium between the 4 and 6 membered rings and then only under thermal conditions. Accurate determination of an equilibrium constant is prevented by the accompanying side reactions. An equilibrium under our photochemical conditions is not possible because $(\text{Me}_2\text{SiSe})_2$ and $(\text{Et}_2\text{SiSe})_2$ do not absorb at 254 nm.

Ring Contraction in the Presence of D₃. Evidence for Silaneselones.

Photolysis or thermolysis of (Me₂SiSe)₃ (or (Et₂SiSe)₃) in the presence of excess D₃ gives (Me₂SiSe)₂ and 2,2,4,4,6,6,8,8-octamethyl-1,5,7,3,2,4,6,8-trioxa-tetrasil-selenocane (12) (or (Et₂SiSe)₂ and 4,4,6,6,8,8-hexamethyl-2,2-diethyl-1,5,7,3,2,4,6,8-trioxatetrasil-selenocane (13), in good yields (Table II). By analogy to known two atom insertions reactions observed for other R₂Si=X species (X = CR₂, NR, O, S)^{7,18} we postulate the intermediacy of silaneselones 10 and 11 (eq 9):



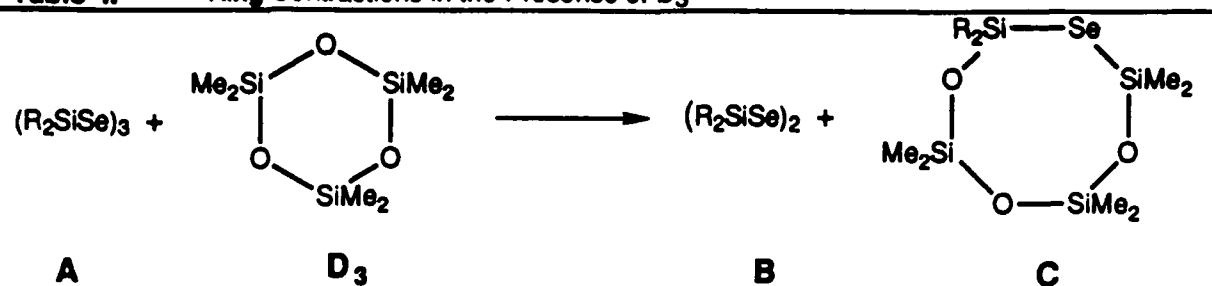
The structures of 12 and 13 can be assigned unambiguously on the basis of ¹³C nmr data. For example, the carbon spectrum of 12 exhibits two singlets at 6.79 and 1.14 ppm respectively. The alternative structure, 14, would have three absorptions.



The data in Table II illustrate important differences in the chemistries of (Me₂SiSe)₃ and (Et₂SiSe)₃. While (Me₂SiSe)₃ is more stable with respect to ring contraction than (Et₂SiSe)₃ (Table I), (Me₂SiSe)₃ is a far better source of a silaneselone than is (Et₂SiSe)₃.

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- 18 a) Golino, C. M.; Bush, R. D.; On, P.; Sommer, L. H. *J. Am. Chem. Soc.* **1975**, *97*, 1957.
 b) Golino, C. M.; Bush, R. D.; Sommer, L. H. *J. Am. Chem. Soc.* **1975**, *97*, 7371.
 c) Okinoshima, H.; Weber, W. P. *J. Organomet. Chem.* **1978**, *149*, 279.
 d) Parker, D. R.; Sommer, L. H. *J. Am. Chem. Soc.* **1976**, *98*, 618.

Table II Ring Contractions in the Presence of D₃



Expt ^a	R	D ₃ /A	Conditions	C/B	% recov'd Se as B and C
1	Me	20/1	254 nm/hexane	2.40/1	80
2 ^b	Me	100/1	254 nm	>100/1	60
3	Me	20/1	225°/decane	3.00/1	65
4 ^b	Me	100/1	225°	>100/1	70
5	Et	8/1	254 nm/hexane	0.33/1	81
6	Et	20/1	254 nm/hexane	0.55/1	85
7 ^b	Et	100/1	254 nm	3.00/1	85
8	Et	30/1	225°/decane	0.65/1	84
9 ^b	Et	100/1	225°	2.70/1	72

^aAll reactions showed complete consumption of starting material

^b Experiments run without solvent.

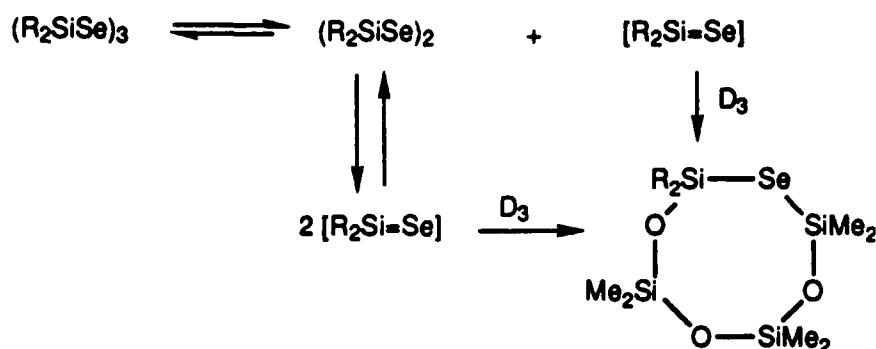
The experiments with D₃ affect overall silaneselone production. For example, when the ratio of D₃ to (Me₂SiSe)₃ is 100:1, <1% of (Me₂SiSe)₂ is detected (Expts 2 and 4). On the other hand, when a D₃:(Et₂SiSe)₃ ratio of 100:1 is used, the product mixture contains >70% (Et₂SiSe)₂ (Expts 7 and 9). While the product distribution may be affected by relative trapping efficiencies, i.e., the smaller dimethylsilaneselone (10) probably reacts faster with D₃ than diethylsilaneselone (11), the reactivities of the cyclodisilselenanes play a key role because they are sources of silaneselones. When (Me₂SiSe)₂ and a 12 fold excess of D₃ is refluxed in hexane for 60h, no selenocane is observed, but (Me₂SiSe)₃ is obtained in 22% yield. This suggests that (Me₂SiSe)₂ is a better trap for the silaneselone than D₃ but (Me₂SiSe)₂ is approximately ten times more reactive (Table III). In these reactions, cyclodisilselenanes are not traps of chemical consequence, since any six membered ring which is formed should fragment to give silaneselone.

Table III. Thermolysis of $(R_2SiSe)_2$ with D_3

$(R_2SiSe)_2 + D_3 \longrightarrow \text{Cyclodisilselenane (6-membered ring: } R_2Si-Se-SiMe_2-O-SiMe_2-O \text{)}$				
B		C		
R	D_3	Conditions	% Yield C	% Conversion of B
Me	12/1	225°/decane/48h	70	90
Et	12/1	250°	5	9

We propose the following pathways for the thermal ($> 200^\circ$) reactions of hexaalkylcyclotrisilselenanes in the presence of D_3 (Scheme 4). The reaction begins with the extrusion of dialkylsilaneselone by the cyclotrisilselenane. The silaneselone once formed may dimerize, insert into D_3 giving the selenocane or insert into newly formed cyclodisilselenane reforming starting material. We see no evidence of insertion of silaneselone into cyclotrisilselenane to produce cyclotetrasil-selenane (in similar experiments with cyclotrisilthianes no cyclotetrasilthianes were observed^{7,8}). Cyclodisilselenane formed in the reaction is also capable of extruding silaneselone (e.g., $(Me_2SiSe)_2$ is a more efficient source of silaneselone than $(Me_2SiSe)_3$).

Scheme 4

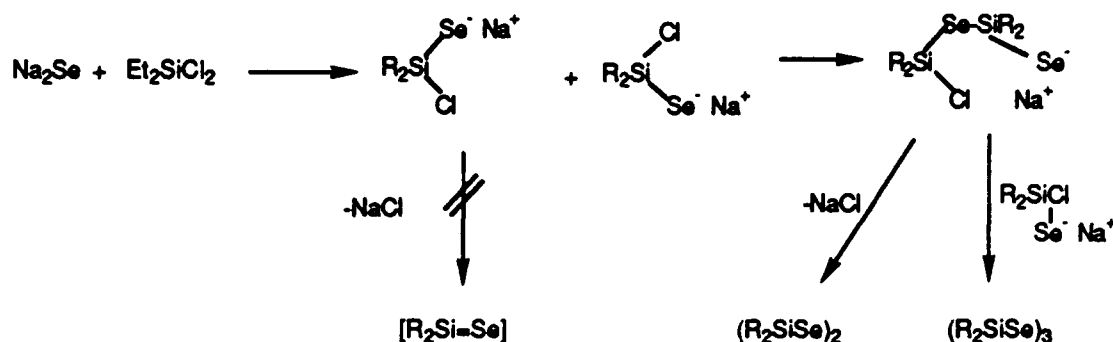


When $(Et_2SiSe)_3$ is photolyzed or thermolyzed in the presence of triethylsilane no Si-H insertion is observed. The only observable product is $(Et_2SiSe)_2$ in 90% yield. This indicates that the silaneselone does not readily insert into Si-H bonds under these conditions, and is further evidence that silylene formation is not an important pathway in the decomposition of alkylated cyclotrisilselenanes.

No cycloaddition reactions between silaneselones and dienes or alkenes were observed. When $(Et_2SiSe)_3$ is photolyzed in a 12-fold excess of cyclohexene, or heated (225°) in a 12-fold excess of anthracene, the only product observed is $(Et_2SiSe)_2$ in approx. 90% yield.

We also investigated the possibility that silaneselones might be intermediates in the synthesis of cyclosilselenanes by treating Et_2SiCl_2 with sodium selenide in the presence of D_3 . No selenocanes were detected. This suggests that ring formation occurs primarily through bimolecular reactions involving ionic intermediates (Scheme 5).

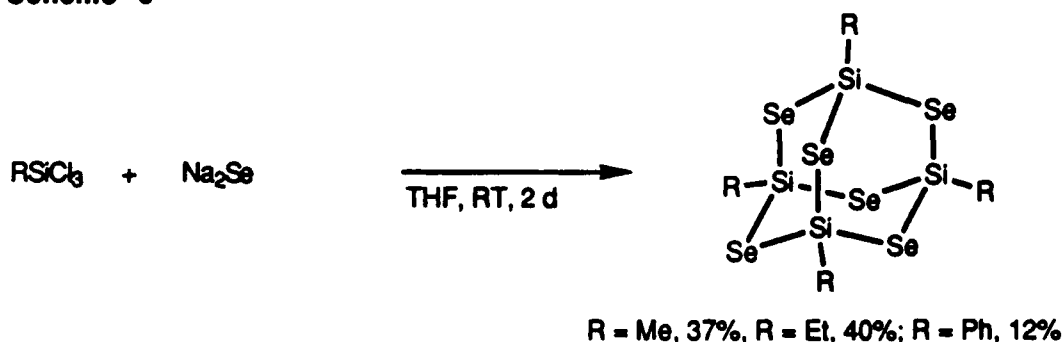
Scheme 5



Tricyclicsilselenanes

Several compounds containing Group IV and Group VI elements with the adamantane type cage structure are known. There are, however, only two references describing the synthesis of a Si-Se cage system.^{19,20} We have found that when RSiCl_3 ($\text{R} = \text{Me, Et, Ph}$) is added to sodium selenide, made *in situ* from sodium, selenium, and a catalytic amount of naphthalene, the corresponding tricyclo[3.3.1.1^{3,7}]tetrasilselenane is produced (Scheme 6).

Scheme 6



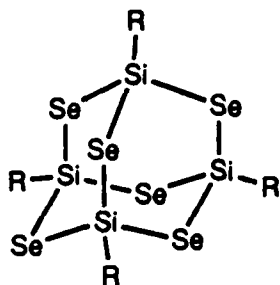
All three compounds are white, crystalline solids which decompose over the course of hours if left in air. Decomposition produces a red solid, presumably including amorphous elemental selenium.

There are two possible structures for a $(\text{RSi})_4\text{Se}_6$ cage system given below as A and B. ^1H , ^{13}C , and ^{29}Si NMR data will be nearly identical for the two structures except for slight differences in

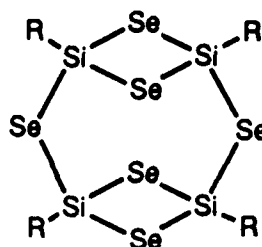
¹⁹ Forstner, J. A.; Muttarties, E. L. *Inorg. Chem.* 1966, 5(4), 552.

²⁰ Haas, A.; Hltze, R.; Kruger, C.; Angermund, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* 1984, 39B(7), 890.

chemical shifts. However, ^{77}Se NMR will discriminate between structures. For A, the ^{77}Se NMR spectra should exhibit one absorption. In B, the ^{77}Se NMR spectra should show two peaks, one signal for the Se atoms in the four-membered rings and another for the Se atoms bridging the two four-membered rings. We observed only one peak in the ^{77}Se spectrum confirming A as the structure.



A

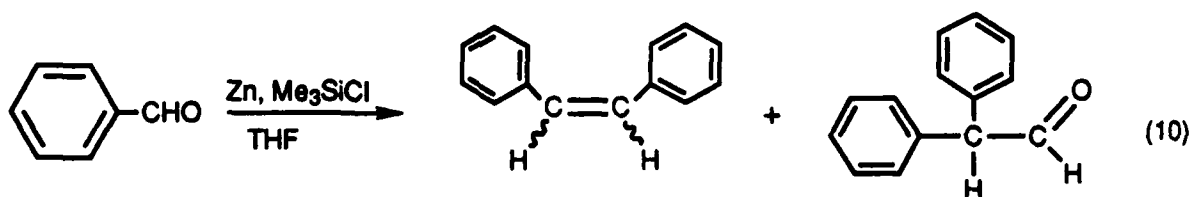


B

Organosilicon Sonochemistry

Silicon Promoted Coupling of Carbonyls

The reductive coupling of carbonyls is of great interest because they offer a more convenient route to pinacols. Recently we reported that ultrasonic waves improved the reductive silylation of some dicarbonyls in the presence of trimethylchlorosilane and zinc to give bis(trimethylsiloxy)-alkenes.²¹ We have since found that aromatic substituted carbonyls can be easily dimerised to give alkenes and/or pinacolones in the presence of trimethylchlorosilane and zinc (eq 10). Ultrasound



irradiation of the reactions increases the yield 5-100% compared to stirring at the same temperature. For arylsubstituted ketones and aldehydes, the dominant reaction pathway is reductive coupling of the acyl carbons to give A, B and/or C. Each of these products can be obtained in synthetically useful yields by manipulating the stoichiometry of the reactants.

There is a report that ring opening of THF by trimethylchlorosilane in the presence of metal oxides.²² In our study, when the reaction time is longer than 4h at 35 $^{\circ}$ C in the presence of zinc and

²¹ So, J.-H.; Park, M.-K.; Boudjouk, P. *J. Org. Chem.* 1988, 53, 5871.

trimethylchlorosilane, THF reacts with trimethylchlorosilane to produce ring cleavage products, one of them is 4-chlorobutoxytrimethylsilane which was detected to GC/MS. 1,4-dioxane or diethylether do not react with even longer reaction time.

New Catalytic Processes Involving Silicon

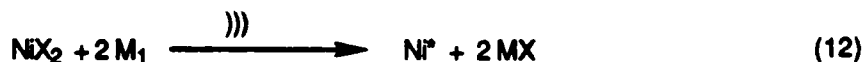
Hydrosilation

Simple Alkenes and Alkynes

The hydrosilation of alkenes and alkynes (eq 11) is the most important industrial method for preparing all but the simplest silicon monomers. Typically, the most effective catalysts for this



reaction are soluble complexes of platinum and rhodium. These catalysts produce very high yields of the desired products under mild conditions but suffer from the costly drawback of being unrecoverable. The loss of these precious metals results in a significant increase (~ \$ 0.12/lb) in the cost of organosilanes. Heterogeneous catalysts are invariably cheaper because of the nearly infinite turnover rate they achieve because they are recoverable. Unfortunately, for silicon, there have been no highly efficient catalysts for the hydrosilation reaction. We have addressed this problem and have succeeded in developing a very effective and inexpensive catalyst for the reaction. We found that highly activated nickel will catalyze the reaction to produce high yields of adduct under very mild conditions.²³ We generate this activated nickel by the simple procedure of reducing a nickel halide to a nickel dispersion with an alkali metal (eq 12):



This procedure can take as little as ten minutes at room temperature. Isolation of the powder is not necessary because the olefin and the hydrosilane can then be added directly and reaction in eq 11 will proceed. Yields are typically >90% and the catalyst is totally recoverable showing no loss in activity for ten cycles. Scanning electron microscopy of the sonicated nickel shows significant pitting of the surface. The particles are very small (10 - 25 microns in diameter) and very rough in texture. The method is mild and broad in scope. We have found the catalyst is also effective for some functionalized olefins such as acrylonitrile and methylacrylate although mixtures of isomers are often obtained.²⁴ These reactions are under study.

²² So, J.-H.; Park, M.-K.; Boudjouk, P. submitted, So. J.-H. *Ph. D. Thesis*, 1989, North Dakota State University, Fargo, North Dakota 58105

²³ Boudjouk, P. U.S. Patent No. 4,827,009, 1989.

²⁴ Jacobsen, J. *M.S. Thesis*, 1989, North Dakota State University, Fargo, North Dakota 58105.

Activated Olefins

The hydrosilation of activated olefins is of continuing interest from two perspectives: 1) many of the silylated derivatives are commercially important products, and, 2) the activating groups cause unusual regioselectivity leading to interesting mechanistic questions. We have undertaken a program to investigate the hydrosilation of selected functionalized olefins in an effort to improve on the literature methods of preparation of the silicon derivatives and to gain insights into the mechanism of these hydrosilation reactions.

We have developed a new, effective and inexpensive catalyst for the selective β -hydrosilation of acrylonitrile (eq 13).²⁵ The reaction is significant because it produces the β isomer totally uncontaminated by the α isomer. The α isomer is unstable and of no synthetic or commercial value.



The β isomer on the hand is a key intermediate in a number of commercially important processes such as the synthesis of silylallylamines. Our catalyst system is totally recoverable and does not diminish in reactivity when recycled. We are now engaged in the optimization of regioselective hydrosilations of acrylate, an important monomer in polymerization.

Reductive Coupling of Hydrosilanes

The formation of silicon-silicon bonds from simple silanes is, practically speaking, limited to variations of the Wurtz coupling reaction.²⁶ Recently, however, there has been some success in Si-Si catenation using complexes of Groups 4, 7, and 8.²⁷ In this communication we report the catalysis of dehydrogenative coupling of hydrosilanes by activated nickel and spectroscopic evidence in support of an intermediate with a Ni-H linkage.

Freshly prepared metal powders have found numerous uses in synthesis because of their significantly increased reactivities compared to commercially available powders.²⁸ Moreover, the rate of generation and the activities of these powders can be significantly enhanced when they are

²⁵ Rajkumar, A. B.; Boudjouk, P. *Organometallics* 1989, 8, 549..

²⁶ For an authoritative review on polysilanes see: Miller, R. D.; Michl, J. *Chem. Rev.* 1989, 89, 1359.

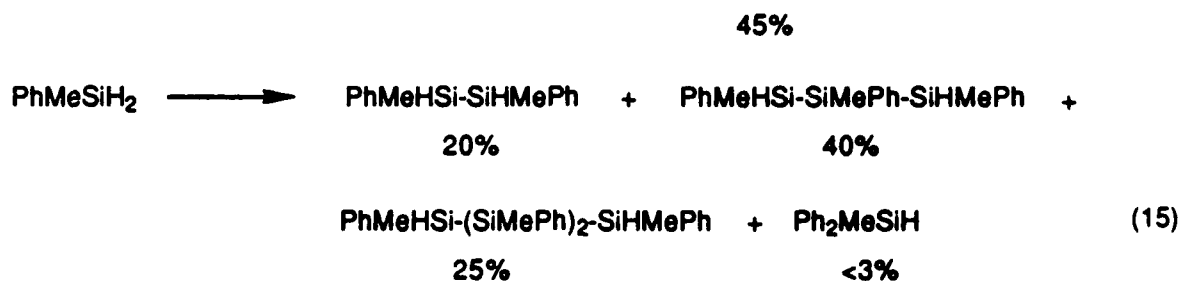
²⁷ a) Chang, L.S.; Corey, J.Y.; *Organometallics* 1989, 8, 1885; b) Aitken, C.; Harrod, J. F.; Gill, U. S.; *Can. J. Chem.* 1987, 85, 1804; c) Campbell, W. H.; Hilty, T.K.; Yurga, *Organometallics* 1989, 8, 2615; d) Pannel, K. H.; Vincenti, S. P.; Scott, R. C. III *Organometallics* 1987, 6, 1593; and, e) Brown-Wensley, K. A. *Organometallics* 1987, 6, 1590; e) Woo, H.-G.; Tilley, T. D. *J. Am. Chem. Soc.* 1989, 111, 8043.

²⁸ Rieke, R. D.; Burns, T. P.; Wehmeyer, R. M.; Kahn, B. E. *High Energy Processes in Organometallic Chemistry*; Suslick, K.S.; Ed.; ACS Symposium Series 333; American Chemical Society, Washington, D.C. 1987; Chapter 14.

produced in an ultrasonic field.²⁹ We have found that nickel powder, freshly prepared from nickel iodide and lithium dispersion in the presence of ultrasonic waves, not only catalyzes the hydrosilation of olefins and alkynes as described above but also catalyzes the formation of Si-Si bonds from phenyl-substituted hydrosilanes. Diphenylsilane, for example, when treated with one mole percent each of activated nickel and triphenylphosphine at 80° gives a 45% yield of *sym*-tetraphenyldisilane in 3-4 h.³⁰ (eq 14).



No higher polysilanes were observed. However, when phenylmethylsilane is used under the same conditions, a broader distribution of products is obtained (eq 15):



By comparison, we found, as did others³¹, that the Wilkinson catalyst promotes disproportionation to much larger extent, e.g., 30% Ph₂MeSiH is formed from PhMeSiH₂, apparently at the expense of catenation since no tetrasilane is observed. While it is premature to set down a detailed mechanism, we suggest that oxidative addition of the hydrosilane³² to nickel followed by reductive elimination of Si-Si species and H₂ is a reasonable pathway and is consistent with our observations (Scheme 7):

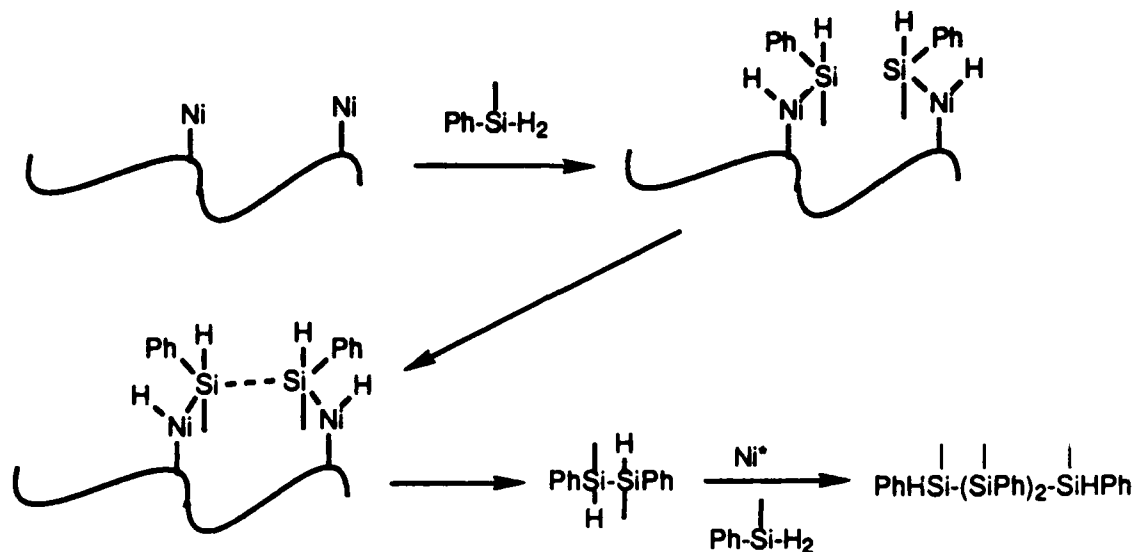
²⁹ Boudjouk, P.; Thompson, D. P.; Ohrborn, W. H.; Han, B.-H. *Organometallics*, 1986, 5, 1257; For a general treatment of the effects of ultrasonic waves on the reactions of metals with organic substrates see: Boudjouk, P. *High Energy Processes in Organometallic Chemistry*; Suslick, K. S., Ed.; ACS Symposium Series 333; American Chemical Society: Washington, DC, 1987; Chapter 13.

³⁰ All yields are gc yields using an internal standard and when combined with unreacted starting material the mass balance for silicon is >90%.

³¹ Ojima, I.; Inaba, S.-I.; Kogure, T.; Nagai, Y. *J. Organometal. Chem.* 1973, 55, C7.

³² Reactive intermediates resulting from oxidative addition of the Si-H bond to metals have been frequently invoked in hydrosilylation reactions (Armitage, D. A. in *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W. Eds.; Pergamon Press: Oxford, England 1982; Vol. 2, Chapter 9.) and in homogenous dehydrogenative coupling reactions (see ref 2)

Scheme 7



Vibrational spectroscopy provides a convenient method of following the formation of these bonds. We have examined the Raman spectra of activated nickel suspensions exposed to phenylsilane in an effort to shed light on the mechanism. In a complex matrix such as the activated nickel suspension, the low frequency region is obscured by a variety of absorptions prohibiting unambiguous identification of the Si-Ni band. In contrast, the frequency regime characteristic of Ni-H bond formation (1800 - 2000 cm⁻¹)³³ is relatively free of normal hydrocarbon frequencies.³⁴

The Raman spectrum of activated nickel exposed to normal protio-phenylsilane, PhSiH₃ is presented in Figure 1A. For comparison, the spectrum of trideutero-phenylsilane, PhSiD₃, is given in Figure 1B. The important difference between the two spectra is the presence of a strong band at 1947 cm⁻¹ in 1A and its conspicuous absence and replacement with a less intense absorption at 1543 cm⁻¹ in 1B. An isotopic shift of this sign and magnitude is consistent with simple replacement of H in a nickel hydride with D.³⁵ Thus we assign the band at 1947 cm⁻¹ to the Ni-H vibration. This is the first spectroscopic evidence for the oxidative addition of silicon hydride to nickel.

³³ Longoni, G.; Chini, P; Cavalieri, A. *Inorg. Chem.* 1976, 12, 3025.

³⁴ Other bands can complicate assignments in this area however. We have demonstrated that, under the appropriate conditions, activated nickel can degrade tetrahydrofuran and diethyl ether to produce species with bridging and terminal nickel carbonyl groups. Parker, W. L.; Rajkumar, A. B.; Boudjouk, P. *J. Am. Chem. Soc.* accepted for publication

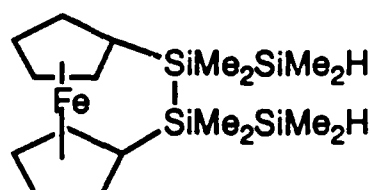
³⁵ Ibach, H.; Mills, D. L. *Electron Energy Loss Spectroscopy and Surface Vibrations*; Academic Press: New York, 1982; Chapter 4.

Polysilanes

We have successfully prepared some essential precursors to the first silicon based star polymers. The approach we have taken is synthesize the central unit and attach polysilane arms to the unit as shown below:

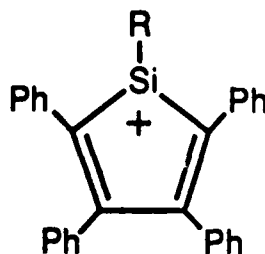


These star polymers, regardless of molecular weight, should be very interesting precursors to silicon carbides. Functionalization is also possible that will allow attachment of a wide variety of groups. We are particularly interested in incorporating metals into the polysilane backbone. Recently we have attached ferrocene units to oligosilanes in the hope of generating new and novel units for metal incorporated polysilanes:



Silacanium Ions

Trivalent silicon cations (sometimes called silacanium ions or silylenium ions) are rare even though the carbon analogs are ubiquitous. We wish to enlarge this area of organosilicon chemistry because of the promise of these reagents as potential Lewis Acid Catalysts and because they will undoubtedly open new reaction pathways for silicon compounds. We have very promising results in our study of siloles. At this point, we have demonstrated, in collaboration with Joseph Lambert of Northwestern University, that the silole ion below is highly dissociated in solution.



In recent months we have devoted our efforts to isolating crystals of this cation with an appropriate counter ion.

Trimethylchlorosilane as a Dehydrating Agent

Although there are several methods for preparing anhydrous metal halides,³⁶ thermal and chemical methods of removing water from hydrated metal halides are the most frequently employed. The pyrolysis of metal halide hydrates has been studied extensively and can lead to anhydrous salts although temperature control is important for many hydrates because water is released stepwise and mixtures of hydrates can be obtained.³⁷ Dehydrating agents such as 2,2-dimethoxypropane and thionyl chloride are efficient and have been widely used although each has some disadvantages.

2,2-Dimethoxypropane, for example, reacts with metal hydrates producing acetone and methanol which often complex to the metal halide³⁸ (eq 16). Both groups are barriers to further reactions with active metals and many organometallic reagents.



Thionyl chloride reacts with water evolving hydrogen chloride and sulfur dioxide as gases thereby reducing the opportunity for contamination of the product halide (eq 17).³⁹ However, thionyl chloride is a severe lachrymator that must be freshly distilled before use.



Moreover, it must be used in excess to achieve reasonable rates and removing the last traces of thionyl chloride is sometimes difficult.

We have discovered that trimethylchlorosilane is a quick and efficient dehydrating agent for metal chloride hydrates that is free of the drawbacks mentioned above (eq 18).



Solvated and unsolvated anhydrous metal chlorides can be prepared conveniently and in very high yields under mild conditions *via* dehydration of metal chloride hydrates with trimethyl-

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³⁷ a) Hassanein, M. *Thermochim. Acta* 1983, 61, 121. b) Williams, J. R.; Wendlandt, W. W. *Thermochim. Acta* 1973 7, 275. c) Grindstaff, W. K., Fogel, N. *J. Chem. Soc., Dalton*, 1972, 1476.

³⁸ Starke, K. *J. Inorg. Nucl. Chem.*, 1959, 11, 77.

³⁹ a) Shamir, J. *Inorg. Chim. Acta*, 1989, 156, 163. b) Pray, A. R. *Inorg. Syn.* 1957, 5, 153.
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chlorosilane. When THF is used as a solvent, the metal chloride is obtained as a tetrahydrofuranate complex with the exception of barium chloride which is isolated as the simple salt. The high solubilities of metal chloride hydrates in THF result in homogeneous reactions and shorter reaction times than when neat trimethylchlorosilane is used. With THF, the reactions were complete in less than 1 h while reactions in neat trimethylchlorosilane were heterogeneous and required 3-4 h of refluxing. Our results are summarized in Table IV.

Table IV. Dehydration of Metal Chlorides with Trimethylchlorosilane

$MX_n \cdot H_2O$	Color	Product	Color	Yields(%)
$CrCl_3 \cdot H_2O$ ^{a,b}	green	$Cr(THF)_3Cl_3$	purple	89%
$CuCl_2 \cdot 2H_2O$ ^b	blue	$Cu(THF)_{0.8}Cl_2$	yellow	95%
$BaCl_2 \cdot 2H_2O$ ^b	white	$BaCl_2$	white	95%
$ZnCl_2 \cdot n(H_2O)$ ^c	white	$Zn(THF)_2Cl_2$	white	71%
$ZnCl_2 \cdot n(H_2O)$ ^{c,d}	white	$ZnCl_2$	white	96%
$BaCl_2 \cdot 2H_2O$ ^d	white	$BaCl_2$	white	95%
$CuCl_2 \cdot 2H_2O$ ^d	blue	$CuCl_2$	yellow	90%
$CoCl_2 \cdot 6H_2O$ ^{d,e}	red	$CoCl_2$	blue	95%
$FeCl_3 \cdot 6H_2O$ ^{d,e}	orange	$FeCl_3$	dk. green	95%

a) Requires THF for complete dehydration

b) Approximate composition of reaction mixture: 30 mL trimethylchlorosilane / 20 mL THF / 10 mmol hydrate

c) Samples of hydrated $ZnCl_2$ were made by adding water (10% by weight) to anhydrous $ZnCl_2$.

d) Dehydrations were performed in trimethylchlorosilane: 30 mL / 10 mmol hydrate.

e) $FeCl_3$ and $CoCl_2$ react with THF, reactions must be run in neat trimethylchlorosilane.

The formation of HCl and of the very strong silicon-oxygen bonds in hexamethyldisiloxane drive the reaction. The reactions are easily monitored by characteristic color changes and workup is relatively simple because the byproducts have low boiling points (HCl (-84°C), trimethylchlorosilane (57°C), hexamethyldisiloxane (101°C)) and are efficiently removed under reduced pressure. The THF adducts were characterized by IR spectroscopy by comparing the C-O-C symmetric and asymmetric stretches with those reported by Kern.^{40a} Excellent agreement was obtained in each case.

Some salts could not be dehydrated in THF. Iron(III) chloride and cobalt (II) chloride dihydrate for example, polymerize THF^{40a} and must be prepared using neat trimethylchlorosilane. In both cases, nearly quantitative yields of the anhydrous salt were obtained. Hydrated zinc chloride, which

⁴⁰ a) Kern, R. J. *J. Inorg. Nucl. Chem.* 1962, 24, 1105. b) Jones, P. J.; Hale, A. L.; Levason, W.; McCullough, jr., F. P. *Inorg. Chem.*, 1983, 22, 2642.

we prepared by adding 10 weight percent water to the anhydrous chloride because well-defined hydrates are not commercially available, was very efficiently dehydrated in neat trimethylchlorosilane to give 96% zinc chloride. In contrast, the THF / trimethylchlorosilane mixture afforded a comparatively modest 71% yield of the tetrahydrofuranate. Chromium (III) chloride hexahydrate, on the other hand, could not be completely dehydrated in neat trimethylchlorosilane and required THF for an efficient reaction giving 89% yield of chromium (III) chloride tris(tetrahydrofuran).

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Principal Investigator:	Dr. Philip Boudjouk
Senior Personnel	Dr. Carolyn Osterberg Dr. Daryl Osterkamp Dr. Jerome Knoblich
Junior Research Personnel	Mr. Steven Bahr Mr. Eric Black Mr. Brian Hauck Mr. John Jacobsen Mr. Rajkumar Kumarathanan Mrs. Amirthini B. Rajkumar Mr. Upasiri Samaraweera Mr. Timothy Splinter Mr. Robert Soular Ms. Lisa Hasvold Mr. Dean Seidler Mr. Sean Ouyang

Publication List of the Principal Investigator

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